(WO/2003/072664) INK COMPOSITIONS CONTAINING LANTHANIDE COMPLEX

Note: OCR Text

INK COMPOSITIONS CONTAINING LANTHANIDE COMPLEXES The present invention relates to ink comp lanthanideliX complexes, a system for marking items with a hidden mark and a method for providing hidden

There is a need for applying hidden marks which can only be revealed under UV exposure on a variety of ar reasons.

Thus, security markings are needed on envelopes, checks, bank-bills shares, securities, stamps, identity ca certificates etc.

Textiles are also furnished with such covert designs which may act as security markings or as special decora become visible under UV radiation.

WO 97/10307 discloses a jet ink composition suitable for marking on white or light coloured substrates comp and a fluorescent colorant which is a rare earth metal organic chelate. These fluorescent colorants are excita radiation in the range of from about 275 nm to about 400 nm and fluoresce in the visible range. However, the luminescence and the quantum yield do not meet the most superior requirements.

It is therefore an object of the present invention to provide an ink composition comprising a colorant which is unaided eye but yields a strong luminescence under UV exposure and which composition can be used for al applications on various substrates such as textiles including leather, cellulosic materials, metals, plastic mate substrates coated with an oligomeric or polymeric matrix and other porous materials.

The invention relates to an ink composition containing (a) a compound of formula I Lm-Ln3+ (Ch-) n (1), whe lanthanide, Ch-is a negatively charged ligand containing at least one UV absorbing double bond, n denotes number from 1 to 4, in case n is 3, m denotes a number from 1 to 4 and L is a neutral monodentate or polyde oxygen-or sulfur-containing UV absorbing ligand with the exception of 2, 2'-bipyridyl or, in case n is 4, m den

single-charged cation; and (b) a liquid ink carrier.

The compounds of formula I can basically contain any monodentate or polydentate nitrogen-, oxygen-or sulf absorbing ligand such as, for example, unsubstituted or substituted pyridine, pyrazine, quinoline, aniline, phe terpyridine, imidazole, benzimidazole, bisimidazole, bisbenzimidazole, pyrimidine, bipyrimidine, naphthyridin oxazol, bisoxazole, oxazoline, bisoxazoline and substituted derivatives thereof and all relevant (poly) N-oxid cited ligands.

Since L can be a polychelating ligand, like for example 4, 4'-bipyridyl, the compounds of formula I and 11 inc chelate, such as for example the compound of formula (XIV), containing two M"'- (diketone) 3 or M"- (carbox connected via a bidentate ligand : Preferred ink compositions contain as component (a) a compound of form wherein Ln represents a lanthanide, n denotes 3 or 4, m denotes a number from 1 to 4 in case n is 3, m den to 4 and L is a neutral monodentate or polydentate nitrogen-, oxygen-or sulfur-containing UV-absorbing ligar of 2, 2'-bipyridyl or, in case n is 4, m denotes 1 and L is a single-charged cation, R2, is hydrogen or C1-C6al are each independently of the other hydrogen, C1-C6alkyl, CF3, C5-C24aryl or C4-C24heteroaryl.

Preferably L is a nitrogen-containing ligand.

Particularly preferred are compounds of formula 1, wherein L is a compound of formula V, VI, VII, VIII or IX w R6 are each independently of the other hydrogen, halogen, C1-C8alkyl, C5-C24aryl, C6-C24aralkyl, C1-C6a a cyclic amino group and R7 is hydrogen, C1-C6alkyl, C5-C24aryl or C6-C24aralkyl.

Alkyl groups as substituents R, to R7 can be straight-chain or branched. Examples that may be mentioned a propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n- pentyl, neopentyl, isopentyl, n-hexyl and isohexyl.

Alkoxy groups as substituents R4 to R6 can be, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-but

Examples of C5-C24aryl groups are phenyl, tolyl, mesityl, isityl, diphenyl, naphthyl and anthryl.

Phenyl is preferred.

Heteroaryl group preferably contain 4 or 5 C atoms and one or two heteroatoms selected from 0, S and N. E furanyl, thiophenyl, oxazolyl, thiazolyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolyl, purinyl or chinolyl.

Aralkyl groups as substituents R4 to R7 can be, for example, benzyl, 2-phenylethyl, tolylmethyl, mesitylmeth chlorophenylmethyl.

Suitable dialkylamino groups are, for example, diethylamino, diisopropylamino, di-n-propylamino, N-methyl-N particular, dimethylamino or pyrrolidino.

Suitable cyclic amino groups are pyrrolidino and piperidino.

Halogen atoms as substituents R4 to R6 are preferably fluorine, chlorine or bromine, but in particular chlorin

Preferred ink compositions according to the invention contain as component (a) a compound of formula 1, w compound of formula V, VI, VII, VIII or IX wherein R4, R5 and R6 are hydrogen, methyl, dimethylamino or py

Preferred components (a) are compounds of formula I wherein Ln is Eu, Tb or Dy.

Furthermore, compounds of formula II, III or IV are preferred, wherein R, and R3 are methyl, t-butyl, n-pe

R2 in formula II is preferably hydrogen.

Particularly preferred as component (a) are the compounds of formula X, XI, XII, XIII, XIV or XV.

For certain applications it is recommendable to use a combination of different lanthanides, for example Eu a increases the degree of security of the hidden marks, the sophistication of the security level and multiplies th

The compounds of formula I are known, for instance from WO 96/20942, or can be prepared by methods kn example, a ligand such as acetylacetone, benzoylacetone, dibenzoylmethane, dipivaloylmethane, salicylic a caproic acid can be reacted under suitable conditions with a rare earth metal halide such as europium trichlo rare earth metal chelate. Further details can be found in U. S. Patent No.

4,736, 425.

The rare earth metal chelate so obtained can be further reacted with the monodentate or polydentate nitroge containing ligand L thus yielding the rare earth metal chelate compounds of formula II, III and IV.

This reaction is described, for example, in WO 96/20942.

Any suitable ink carrier known in the art of printing compositions, including aqueous and organic carriers and thereof, can be used to prepare the ink compositions of the present invention. The carrier should have suffici compounds of formula I or II and, where appropriate, for the additional ingredients of the ink compositions.

In addition, the carrier should be easily dissipatable from the printed article by evaporation and/or absorption Suitable organic carriers include alcohols, glycols, ether alcohols, sulfoxides, amides, amines, heterocyclic s ethers, esters, nitriles and aliphatic, cycloaliphatic and aromatic hydrocarbons.

Examples of suitable organic solvents are methanol, ethanol, n-propanol, isopropanol, n-butanol, glycerol, et propylene glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, ethylene gl ethoxybutanol, dimethylsulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMA), N- methyl acetone, 2-butanone, diethylether, di-n-propylether, tetrahydrofurane (THF), ethyl acetate, ethyl propionate, n-pentane, n-hexane, cyclohexane, benzene and toluene.

Preferably the ink carrier (b) is an organic solvent, a mixture of two or more organic solvents or a mixture of more organic solvents.

For solvent-based applications it is advisable to employ alcohols, ketones, esters, polyethers or aromatic hyd mixtures of the aforementioned solvents as ink carrier.

Solvents which are miscible with water, like alcohols, glycols, ether alcohols, nitriles, DMSO, DMF, DMA, NM are purposively used for aqueous applications.

Preferred organic solvents are aliphatic alcohols, glycols, cellosolves, dimethylsulfoxide (DMSO), sulfolane, dimethylacetamide (DMA), N-methylpyrrolidone (NMP), aliphatic or aromatic ketones, aromatic hydrocarbon esters and aliphatic polyethers.

Glycerol, ethylene glycol and propylene glycol are especially preferred organic solvents.

The ink compositions according to the invention may additionally comprise one ore more binder resins (c).

The binder resin serves to immobilize or increase the adhesion of the colorant, particularly on non-porous ar example plastic, metallic materials and glassine materials.

Any suitable binder resin can be used. Preferably the binder resin is soluble, dispersible or emulsifiable in th further preferred that the binder resin has sufficient adhesion to the substrate following the dissipation of the

Examples of suitable binder resins include alkyds, acrylic, acrylates, acrylic latexes, epoxy resins, polyvinylp polyurethanes, vinyl resins, polyvinyl acetates, polyvinylalcohol, polyvinylbutyral, PVC, chlorinated rubber, po polyethyleneglycol esters of fatty acids, polyalkenes such as polyethylene, polypropylene and polyoutylene, methylstyrene, copolymers of polyethylene with vinyl acetate, polysulfones, polyesters, polysiloxanes, styren acrylic copolymers, polyacrylics, polyacrylates such as polymethylacrylate and polymethylmethacrylate, nitro cellulose ethers such as methylcellulose and ethylcellulose, and mixtures thereof.

The compositions according to the invention are well compatible with all conventional aqueous and solvent-b formulations known in the art. Some of these printing formulations are commercially available.

In preferred ink compositions according to the invention the binder resin (c) is selected from the group consi polyacrylates, polyurethanes, polyurethane-acrylates, styrene-acrylic copolymers, nitrocellulose and ethylcel

Aqueous ink jet formulations containing polyacrylics, polyacrylates, polyurethanes or polyurethane-acrylates are particularly preferred.

In the compositions according to the present invention the amounts of components (a) and (b) and where ap within wide ranges.

Preferred compositions contain 0.01 to 70.0 %, more preferably 0.05 to 30 % and in particular 0.1 to 10.0 %, component (a) and 30.0 to 99.99 %, more preferably 70.0 to 99.95 % and in particular 90.0 to 99.9 %, by we (b), based on the total amount of components (a) + (b).

High amounts of component (a) are usually well-suited for the ink concentrate in solvent- based applications

The amount of component (c) depends on the printing application which determines the required viscosity ar fixation properties to the substrate. Preferably, the amount of component (c) is 0.5 to 70 %, more preferably particular 1 to 30 %, by weight, based on the total amount of components (a) + (b) + (c).

Further ingredients which may be present in the ink compositions according to the invention are e. g. natural thickeners, dyes, pigments, optical brighteners, acids, bases and/or salts to adjust the pH to the desired valu or cationic surfactants, antifoaming and antifrosting agents, biocides, bactericides, electrolytes, humectants, and fixing agents.

Especially preferred are compositions according to the invention additionally containing (d) one or more colo

Suitable colorants are the well-know pigments and dyes including mixtures of different pigments and dyes.

The ink compositions according to the invention can be prepared by any suitable method known to those of art. For example, the components of the composition can be combined and mixed in a suitable mixer or blen

The present invention further provides a system for marking items with a hidden mark which can only be rev exposure comprising a printing means for printing said mark on said items, wherein said printing means emp composition as described above.

The marking system may additionally include a transport system to carry the items to the printing means. Fo can be carried under the print head of an ink jet printer using a conveyor belt.

The present invention further relates to a method for providing a hidden mark on an object, preferably a texti comprising applying onto said object an ink composition as described above and removing all or substantiall by evaporation or absorption into or onto said object.

The hidden mark can also be hidden into a visible mark, either by overprinting onto a visible mark or by usin formulation, as described in the working examples.

The hidden mark can be made visible by subjecting the object to exciting radiation having a wavelength of fr about 400 nm; the emitted fluorescent radiation is in the visible range, preferably from about 450 nm to abou emission spectrum contains a sharp emission peak.

The invention can be applied in all customary printing applications like flexographic printing, offset printing, s printing, transfer printing and textile printing.

A wide variety of substrates can be marked with the fluorescing colorant according to the invention such as t cotton, leather, silk, polyamide, polyester, mixed fibers, polyacrylonitrile, lycra), celluiosic materials (wood, pa as plastic materials (polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate), po other substrate coated with a receiving polymeric or oligomeric matrix, or which can be coated with a polyme matrix as provided by the binder system (c).

The present invention makes it possible to apply colourless or coloured hidden marks to various colourless, or dark coloured substrates, which can be revealed under UV exposure. The compositions according to the i from analogous prior art compositions by outstanding luminescence quantum yield, long-lasting luminescenc luminescence intensity.

The following Examples illustrate the invention.

Ink Composition A: Concentrate of compound XII in 1, 2-propylene glycol 1 g of compound XII (prepared acc W096/20942) is dissolved in 99 g of 1,2- propyleneglykol under heating at 100°C for 1 hour. The clear yellow cool down and after filtration (clarification) provides the stable ink Composition A which exhibits an intense re under UV light. This concentrate can be further used in either solvent based or aqueous based conventional printing formulations for paper, textile, leather, wood, plastic or other compatible substrates.

Example 1: A colourless aqueous ink-jet ink is prepared by diluting 6 parts by weight of Ink Composition A w
of a standard polyurethane-acrylate aqueous ink-jet ink formulation.

The above described quasi-colourless formulation is printed on white paper, coloured paper, white or colour
in a strong red luminescence under UV exposure.

Example 2: A pigmentary yellow aqueous ink-jet ink is prepared by diluting 1 part of Ink Composition A with
commercial polyurethane-acrylate pigmentary yellow aqueous ink- jet ink formulation.

The above-described yellow formulation was printed on white paper, coloured paper, white or coloured textil
strong red luminescence under UV exposure.

Example 3: A pigmentary red aqueous ink-jet ink is prepared by diluting 3 parts of Ink Composition A with 1 p
commercial polyurethane-acrylate pigmentary red aqueous ink-jet ink formulation. The above-described red
on white paper, coloured paper, white or coloured textiles and results in a strong red luminescence under UV

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